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Review

Porcelain tile: Almost 30 years of steady scientific-technological evolution

E. Sánchez *, J. García-Ten, V. Sanz, A. Moreno

Instituto de Tecnología Cerámica, Asociación de Investigación de las Industrias Cerámicas, Universitat Jaume I, Castellón, Spain

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Abstract

Despite the great global significance of porcelain tile manufacture, the scientific activity in porcelain tile's almost 30-year existence does not match the importance of the business. Although scientific output has been scarce, technological advances have been and still are spectacular, largely driven by machinery builders, in collaboration with glaze and pigment producers.

This paper begins by describing the evolution and distribution of research into porcelain tile per country. The study then reviews the major scientific and technological advances, focusing principally on the developments in raw materials compositions resulting from the introduction of certain key raw materials to enhance composition quality. As the interpretation of unfired body microstructure, and the relation of unfired tile microstructure to processability and to sintered tile microstructure and properties have drawn particular attention from the scientific community, the paper addresses these issues in depth.

The last part reviews the R&D lines which, in the authors' view, will witness further development in the short and medium term and which obviously parallel the technology advances in the product and the manufacturing process.

Keywords: A. Pressing; B. Microstructure-prefiring; B. Microstructure final; D. Traditional ceramics

Contents

1. Introduction

Within the great range of products marketed by the ceramic industry, the developments in porcelain tile have been quite outstanding. Porcelain tile emerged (in its current form) in the late 1970s in Italy [1] as a technical high performer, characterised by a natural look, and more similar in appearance to natural rock or stone than any other ceramic product.

Porcelain tile is a very compact product, vitrified throughout and with extremely low porosity. This low porosity is an essential feature, which provides the material with excellent mechanical and chemical properties, making it frost resistant and therefore extremely serviceable for outdoor flooring and wall cladding in cold climates. It is also highly resistant to chemical substances

* Corresponding author. Tel.: +34 964342424; fax: +34 964342425.
E-mail address: sanchez@itc.uji.es (E. Sánchez).

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and cleaning agents. It resists abrasion well and has a high breakage threshold, making it ideal for highly trafficked and industrial areas, in addition to being easy-to-clean and thus perfect for paving areas where hygiene is of prime importance.

The starting composition is made from a triaxial mixture of clay or kaolin, quartz, and feldspar. The clay fraction helps forming by providing plasticity and dry mechanical strength during processing, and develops mullite and glassy phase during firing. Feldspars develop glassy phase at low temperatures (sodium feldspar being mainly used), assisting the sintering process, and enabling virtually zero (<0.5%) open porosity and a low level of closed porosity (<10%) to be achieved. Quartz promotes thermal and dimensional stability thanks to its high melting point [2,3].

The industrial processing of porcelain tile includes three main stages: (1) wet milling and homogenisation of raw materials, followed by spray-drying of the resulting suspension; (2) uniaxial pressing at 35–45 MPa of the spray-dried powder with a moisture content of 5–7%; (3) fast firing for 40–60 min at 1180–1220 °C to obtain maximum densification.

The search for a new aesthetics has given rise to a broad spectrum of end product finishes, such as polishing. Two common types of porcelain tile finishes are the so-called 'natural' (i.e. as-fired, unpolished) and polished porcelain tile. Natural porcelain tile undergoes no treatment after firing; its appearance is natural, and closely resembles that of rocks or stones found in nature, such as slate, marble, or granite. The polished finish is obtained by grinding and polishing after firing, in order to provide the product with a high-gloss finish like that of polished marble or granite. Porcelain tile is further often machined in order to rectify and square, and/or chamfer the tiles; this is done to enable tile installation with a minimum grout joint, which yields a highly aesthetic finish.

Another kind of product that has made great inroads into the international market in the last 8 years is glazed porcelain tile. Used especially because of its frost resistance and low porosity, the product has become an alternative to other glazed ceramic products and represents yet another opportunity for manufacturers that have so far made unglazed porcelain tiles.

The paper reviews the major scientific and technological advances, focusing particularly on the developments in raw materials compositions, with the introduction of certain key raw materials to enhance composition quality. Moreover, the interpretation of unfired body microstructure, and the relation of unfired tile microstructure to processability and to sintered tile microstructure and properties have drawn particular attention from the scientific community. The latter part of the work reviews the R&D lines which, in the authors' view, will witness further development in the short and medium term and which obviously parallel the technology advances in the product and the manufacturing process.

2. Scientific production in porcelain tile's almost 30-year existence

A simple analysis of the scientific production on porcelain tile in the last 30 years leads to a modest outcome. Only 131 research papers on either the porcelain tile manufacturing process or porcelain tile materials are to be found in the 'World of Science' journals up to 2008. This means that fewer than five papers are published per year on porcelain tile worldwide. The number of patents for the same period is also scant, about 120 documents being available through Matheo patents software.

Table 1
Comparison of global scientific production on porcelain tile and silicon nitride and their respective business until 2008 (estimations of the authors).

	Porcelain tile	Silicon nitride
Number of published papers	131	7889
Estimated annual worldwide production	3900 Mm^2 (78 Mt)	600 t
Estimated annual worldwide business	80,000 M€	280 M€

The analysis probably becomes more telling if the scientific production on porcelain tile is compared with that on silicon nitride, a high technology ceramic material whose evolution (beginning in the 1970s) closely resembles that of porcelain tile. Silicon nitride has attracted much attention in these last few years in the scientific community because of its unique combination of excellent mechanical and thermal properties. Some figures detailing the scientific production on porcelain tile and silicon nitride ceramics and the importance of their respective business are compared in Table 1. The table clearly shows that the scientific production on both materials in no way matches their respective business scope. Indeed, 60 times more papers are to be found on silicon nitride (only considering those found in journals relating to materials) than on porcelain tile, while porcelain tile business (in terms of turnover) is almost 300 times silicon nitride business.

A detailed analysis of the evolution of scientific production (number of papers in the 'World of Science') on porcelain tile, as well as the distribution of this scientific production per country, is presented in Fig. 1. It may be observed that porcelain tile has begun to arouse the interest of the scientific community in the last few years, coinciding with its economic take-off. On the other hand, as might be expected, Italy and Spain, in that order, are the main countries in which porcelain tile has drawn scientific attention, since the principal ceramic tile centres and active researchers are to be found in these countries. Further to be noted is the increasing contribution of countries with an important ceramic tile production, such as Brazil, Turkey, and Iran, in which porcelain tile manufacture is currently growing significantly.

3. Major scientific advances

This section addresses some of the major scientific and technological developments in porcelain tile in its almost 30-year existence. The knowledge involved has been expressed in different scientific and technological papers. However, in many cases, it has only been reflected at industry level or presented exclusively at fairs or exhibitions. The authors are aware of the limited length of this paper, and the difficulty of translating the myriad developments undergone by porcelain tile in this period.

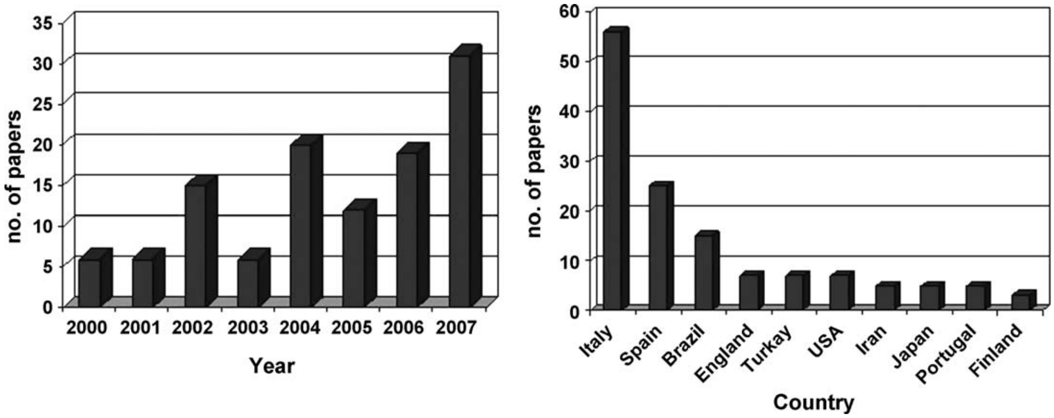


Fig. 1. Evolution and distribution of research into porcelain tile per country.Source: World of Science.

Table 2
Chemical analysis (in wt%) of certain raw materials used in the evolution of Spanish porcelain tile compositions.

Oxide	French feldspar	Turkish feldspar	English clay	Ukrainian clay (low alumina)	Ukrainian clay (high alumina)
SiO_2	75	72	63	65	58
Al_2O_3	15	17	24	23	28
Fe_2O_3	0.30	0.15	1.2	1.0	0.85
TiO_2	0.06	0.30	1.3	1.3	1.4
Na_2O	6.5	9.5	0.2	0.4	0.5
K_2O	1.3	0.35	2.6	2.0	1.9
CaO	1.0	0.3			–
l.o.i	0.2	0.03	6.8	6.4	8.3

The following analysis is divided into the following categories: raw materials and composition design, processing and related problems, and the relationship between porcelain tile microstructure and properties. This is not a random classification, but is related to the scientific production of porcelain tile.

3.1. Raw materials and compositional evolution: the Spanish case

Porcelain tile manufacture began in Spain in 1988 with the production of unglazed, natural (unpolished) and polished tiles. Compositions started using clay from England and to a lesser extent from France and Germany, in quantities ranging from 45% to 60%, together with between 40% and 50% French sodium–potassium feldspar, and to a lesser extent Spanish potassium feldspar. The compositions also contained small percentages of quartz (10%). Since there are no abundant deposits in Spain of clay and feldspar with the characteristics required for porcelain tile production, these raw materials need to be imported [3].

In 1991, Turkish sodium feldspar began to enter these compositions owing to its lower cost, ease of milling, and greater fluxing power than the feldspars that had been used until then. These feldspars were initially imported into Spain in bulk. Later, they began to be micronised by local raw materials suppliers. In time, these feldspars came to displace French feldspars almost entirely. Table 2 lists the chemical analysis of some of these feldspars. Ukrainian clays (see also Table 2) were introduced in 1992, because of their technical advantages, which included high plasticity and fluxing power, and greater whiteness. These differences stemmed from the smaller colouring oxide content and the presence of highly degraded clay minerals (montmorillonite). Accordingly, these clays exhibited greater difficulties in deflocculating, in addition to less consistent characteristics. Even with these drawbacks, the use of such clays became generalised, so that from that time on Spanish porcelain tile compositions were mainly based on Ukrainian clay and Turkish feldspar.

In 1992, manufacturing also commenced of the first porcelain tiles decorated with soluble pigments. The moderate colour intensity achieved with this technique facilitated the emergence of a new type of composition with a higher degree of whiteness than that of the compositions then being used (the L^* co-ordinate increased from 75 to 80 and the b^* co-ordinate decreased from 13 to 8). The new compositions, known as 'white or super white', were obtained by replacing part of the clay with kaolin and introducing small percentages of zirconium silicate (Fig. 2). These changes impaired spray-dried powder pressing behaviour, and increased firing temperature and shrinkage [4].

The use of moderate kaolin contents, which led to mullite formation, along with the introduction of zircon, increased porcelain tile whiteness and opacity, so that the resulting colours became even less intense, though such use significantly improved the colour hue, and the contrast between the coloured and white areas.

Later, in 1998, a new type of Ukrainian clay began to be imported which was characterised by its higher alumina content

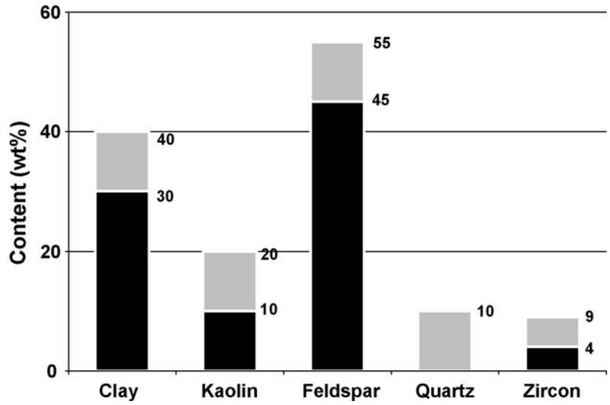


Fig. 2. Typical compositional ranges for 'white and superwhite' porcelain tile bodies.

(high alumina Ukrainian clay). Compared with the (low alumina) clays that had been used until then, these clays displayed greater plasticity and fusibility, as well as a higher degree of whiteness owing to their higher clay mineral content and lower Fe_2O_3 content (see Table 2). However, the rheological behaviour of the spray-drying slurries obtained from these clays entailed greater difficulties, owing to the higher specific surface area (SSA) provided by the presence of small montmorillonite clay mineral contents (the SSA went from 26 to 35 m^2/g). Fig. 3 highlights the differences between the rheological behaviour, evaluated in terms of deflocculation curves, of STD samples of a high alumina Ukrainian clay and a low alumina Ukrainian clay. The use of these clays led to a decrease in the overall clay content in the compositions, which allowed the quartz content to be raised with the ensuing cost savings (for example, today quartz costs 20 €/t while clay costs 60 €/t). Unfortunately, the alumina content of these clays has decreased gradually with time, thus limiting the benefits originally provided.

The increasing manufacture of porcelain tiles by non-European countries, mainly China, with much lower manufacturing costs than those of European producers, forced the Spanish industry to manufacture higher value-added products with a pronounced aesthetic component in comparison with low-price products. As a result, in 2000, suppliers, manufacturers, and research centres devoted significant efforts to designing special compositions with a view to enhancing porcelain tile aesthetic properties. Thus, compositions with great whiteness (known as 'mega whites' and 'hyper whites') began to appear, which were mixed with other, coloured or non-coloured compositions. These compositions have low clay contents and introduce significant percentages of kaolin, making their pressing behaviour more difficult. Frits that devitrified opacifying compounds were also introduced, as well as numerous raw materials typically used in glaze manufacture (zircon, alumina, wollastonite, etc.). In parallel, translucent compositions were developed that imitated the appearance of certain minerals in natural stone tiles. These compositions, with low pigment content, also allowed vivid, clean colours to be obtained. The composition formulations entailed the virtual elimination of clays, and the addition of kaolin, frits, and highly fluxing materials, so that the compositions resembled certain types of ceramic glazes [5,6]. The manufacture of these types of tiles required complex installations prior to pressing, with a multitude of systems for mixing compositions of a different nature and decorating the tiles during their forming phase: micronisers, granulators, mills, mixers, double charge pressing systems and multiple proportioning systems.

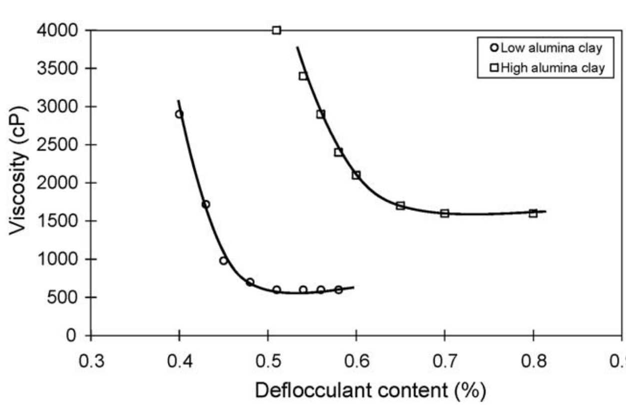


Fig. 3. Deflocculation curves of STD samples of a high alumina Ukrainian clay and a low alumina Ukrainian clay.

At the same time, in 1999, Spain began to produce glazed porcelain tile. The early compositions were based on white-firing stoneware bodies, which were slightly modified to increase the degree of whiteness and raise their fusibility in order to reduce water absorption. Initially, the bodies were not coloured. The success of glazed porcelain tile also attracted traditional porcelain tile manufacturers, who began to glaze their coloured or non-coloured bodies. There were thus two lines of formulations: the first based on glazed white-firing stoneware compositions (lower degree of whiteness), and the second based on unglazed porcelain tile compositions (higher degree of whiteness).

The body-colouring process, which traditionally took place by the wet route (initially in mills and later in tanks), changed dramatically in 2001 with the introduction of the dry colouring technology. The simplicity of this process compared with that of the wet route led to the rapid spread of glazed porcelain tile manufacture with coloured bodies. Fig. 4 shows cross-sectional areas of fired tiles coloured by the wet route and the dry route, in which the difference in pigment distribution can be observed. These compositions needed to display a certain degree of whiteness in order to be coloured, as well as sufficient unfired mechanical strength to offset the negative impact caused by the pigment with this technology. As a result, the use of both organic and inorganic binders to improve the mechanical properties of these bodies became quite commonplace.

Today, the rising cost of imported raw materials owing to high transport costs, as well as the lesser homogeneity of some of these raw materials, is advocating a return to the use of English clays, the increased use of Portuguese clays, and the development of purification processes for local clays. Similarly, it is increasing the use of local mixed feldspar and of highly fluxing materials [7].

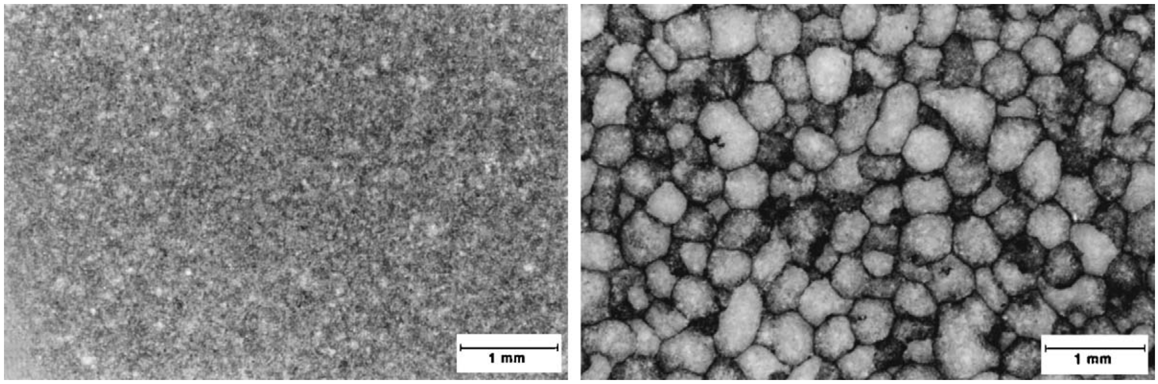


Fig. 4. Optical micrographs of cross-sectional areas of fired porcelain tiles coloured by the wet route (left) and the dry route (right).

3.2. Processing and problems related to the manufacturing process

The effect of porcelain tile composition particle size distribution on the sintering process and on the microstructural characteristics of the fired pieces has been analysed in the literature. Orts and co-workers [8] compare the behaviour during firing of four porcelain tile compositions, milled for different times to obtain different mill oversizes. These researchers conclude that, at the same pressing variables, a greater large particle fraction in the composition (higher reject at 40 μm or smaller degree of milling) yields less porous pieces with larger pores. On the other hand, more vigorous milling (smaller reject at 40 μm) yields more porous pieces with smaller pores. These results agree with the literature [9] and confirm that particle size is directly related to pore size in the green packing. The appearance of the porous texture of tiles (made from the four previously mentioned compositions) fired at maximum densification temperature (T_{max}) and then polished is shown in Fig. 5. The figure also includes the mill reject at 40 μm (R), maximum densification temperature (T_{max}), and final porosity (ε). It can be observed that as the reject at 40 μm rises (degree of milling decreases), more porous pieces are produced with larger-size pores. These findings confirm that the pore size growth occurring during sintering depends on pore size in the green tile, so that fired tile end porosity will depend more on green tile pore size than pore volume.

Spray-drying operating conditions have been extensively analysed in the literature for the production of high-quality spray-dried powders [10,11]. High flow powders of dense, deformable granules are required for producing pressed porcelain tile bodies with adequate microstructure and no defects associated with the pressing operation. García-Ten et al. [11] have shown that granule morphology is directly related to spray-drying suspension characteristics. Thus, the presence of an inner void in the granules can be minimised or eliminated by slightly over-deflocculating the suspensions, increasing solids content or minimising the colloidal particle fraction in the suspension. Processing hollow granules gives rise to tiles with large-sized pores (>100 μm), which indicates that these granules do not totally deform during the pressing stage and that the voids they contain remain in the tiles after firing (Fig. 6). These remaining large pores can readily impair porcelain tile microstructure, and in particular, polished porcelain tile surface quality.

One of the currently most widespread decorating techniques in the manufacture of unglazed porcelain tile is dry colouring of the spray-dried powder used to make the body, which allows

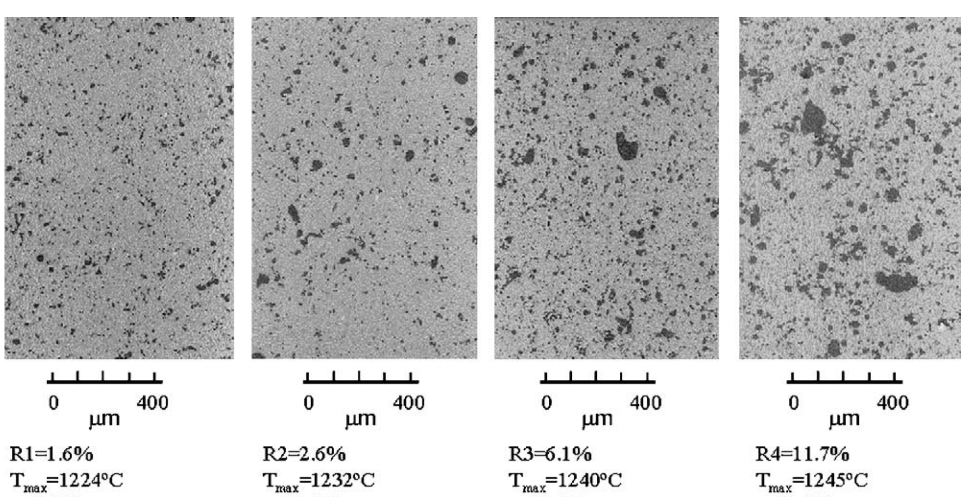
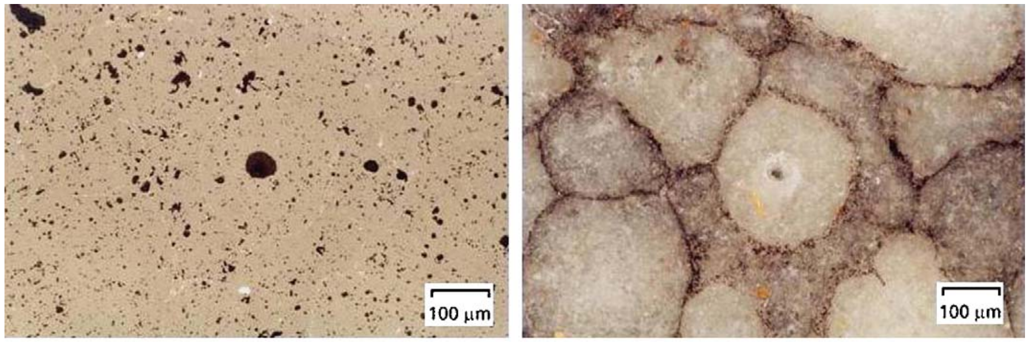


Fig. 5. Cross-sections of pieces fired at T_{max} made from STD porcelain tile compositions with different milling rejects (R1 to R4) (ε denotes fired body porosity).



Temperature 1200 °C (bright field) Temperature 1200 °C (dark field)

Fig. 6. Relation between spray-dried granule void and sintered porcelain tile porosity.

dry colouring to play a key aesthetic role in tile design. The dry colouring process basically consists of mixing the spray-dried powder with a pigment, so that the granules are coated by colorant particles. This process, which is conceptually simple, significantly modifies the microstructure of green porcelain tile bodies, which are made up of a set of areas (spray-dried powder granules deformed during pressing) surrounded by a network of pigment particles. Although this microstructural change is known to influence the green behaviour of the bodies, very few studies have addressed this subject. In a recent study [12], García-Ten et al. examined the influence of some of the variables involved in the dry colouring process on the behaviour of these bodies during the different manufacturing process stages, as well as on the properties of the fired product. The authors observed that dry mechanical strength decreases in the tiles when the dry colouring technique is used. This is because the pigment particles position themselves at the granule boundaries, weakening the intergranule bonds and reducing tile mechanical strength. For a given pigment, the loss of mechanical strength decreases as pigment particle size increases, which must be related to the increased intergranule contact area.

Fired porcelain tile porous texture is the result of tile green microstructure and heat treatment. Fig. 7 schematically depicts the evolution of porcelain tile porosity during firing in terms of apparent porosity (interconnected pores) and closed porosity (occluded pores). Optimum firing temperature is the temperature at which no apparent porosity remains and closed porosity has not yet started to increase. The optimum firing temperature for porcelain tile usually lies between 1190 and 1220 °C. The product's porous texture at this temperature determines its technical properties (see Fig. 16 in Section 3.3).

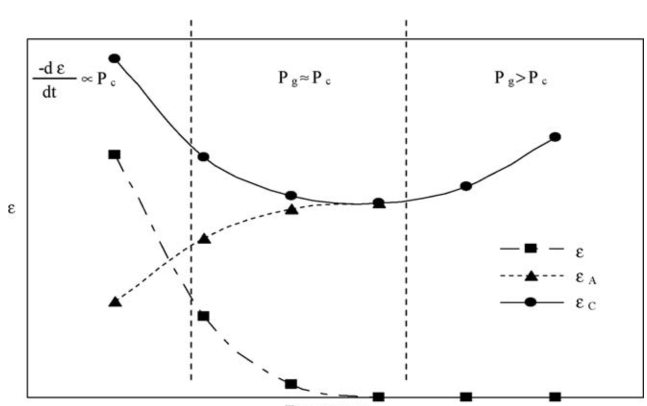


Fig. 7. Evolution of porcelain tile porosity during firing (general example). ε: true porosity, ε_A: apparent porosity, and ε_C: sealed porosity.

Porcelain tile densification involves a liquid phase sintering process [8,13,14]. During firing, at temperatures of about 900–1000 °C, an important quantity of liquid phase begins to form, surrounding the particles and producing a process-driving capillary pressure (P_c) at the contact points. The capillary pressure brings the particles closer together, increasing shrinkage and lowering porosity, while concurrently altering pore size and shape. Raising temperature increases the quantity of liquid phase and lowers porosity. In intermediate states, at around 1180 °C, pores start closing as interpore connections are eliminated. The occluded pores contain air that exerts pressure (P_g) on the pore walls, opposing densification. In advanced process states, above 1200 °C, occluded pore gas pressure is high and counteracts capillary pressure, making the product expand. The sintering rate of this type of material is found from:

$$-\frac{d\varepsilon}{\varepsilon dt} = \frac{3}{4\eta_s}(P_c - P_g) \tag{1}$$

where ε is porosity, η_S is the effective viscosity of the system, P_g is occluded pore gas pressure and P_c is capillary pressure, which is given by $P_c = -2\gamma/r$, where γ is surface tension and r is pore radius.

Fig. 8 depicts the X-ray patterns found for a green and subsequently fired STD porcelain tile composition. The STD tile starting composition contained illite (I), kaolinite (K), quartz (Q) and sodium feldspar-(FNa-albite). The fired body contains mullite (M), quartz, and a small quantity of sodium feldspar. The background in the fired body pattern is observed to be quite high, indicating abundant glassy phase in the fired tile. Quartz peak intensity in the green body is considerably higher than in the fired tile, suggesting partial dissolution of the quartz phase in firing.

Fig. 9 shows the fresh fracture of a STD fired porcelain tile, observed by scanning electron microscopy. The body contains a

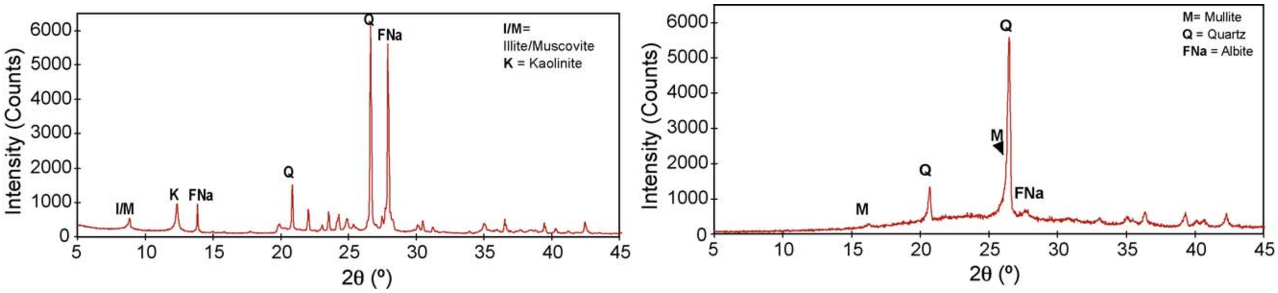


Fig. 8. X-ray diffraction pattern of a STD green porcelain tile body (left) and the corresponding STD fired porcelain tile body (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

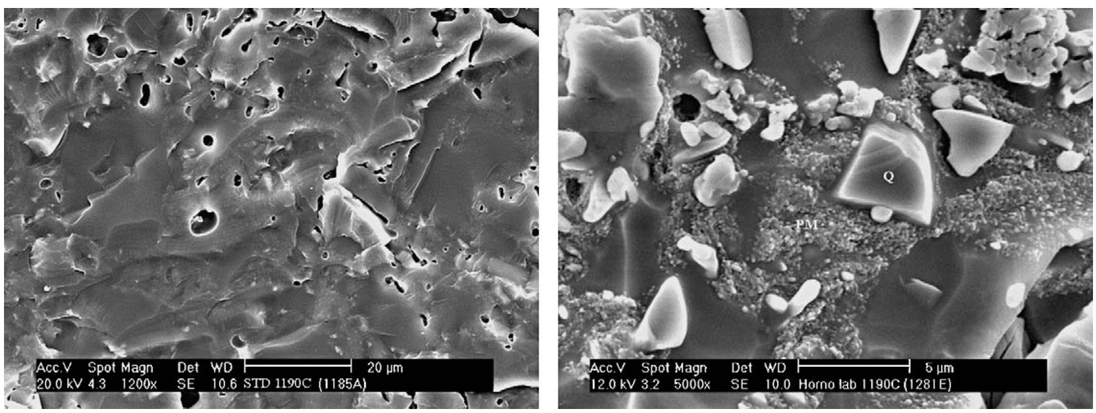


Fig. 9. SEM micrographs of the fracture surface of a STD porcelain tile body fired at T_{max}. Left: as-fractured. Right: etched fracture surface.

few small isolated pores, this test piece being fired at T_{max}. The smooth texture is due to the glassy phase. Etching with HF (Fig. 9) revealed scaly crystals of primary mullite (PM) and quartz (Q) particles, whose rounded edges confirmed partial particle dissolution. Unlike in standard porcelain, needle-like crystals of secondary mullite (SM) are not usually observed in industrially fired porcelain tiles. This is mainly due to the fast firing cycles of porcelain tiles. In addition, the high melt viscosity at maximum density temperature prevents small crystals from dissolving and making the large crystals grow. A recent kinetic study on porcelain tile [15] has shown that primary mullite starts to crystallise at 985 °C, before the sodium feldspar (albite) melting point at ~1100 °C. The study also suggests that internal nucleation is the dominant crystallisation mechanism.

Though porcelain tile compositions resemble porcelain compositions, the manufacturing process differs considerably, especially in the firing stage, since porcelain tile firing cycles are much faster (40–60 min) than porcelain firing cycles (12–24 h). Residual stresses then arise during the porcelain tile manufacturing process owing to rapid industrial cooling. The development of macroscopic residual stress, like that in glass tempering processes, has been recently reported [16]. This research has shown that when the level of residual stress increases as a result of faster cooling in the material's viscoelastic temperature range ($T > \sim 700$ °C), porcelain tile mechanical strength rises, as in a glass tempering process. The existence of thermal gradients between the surface and the interior of the piece during the allotropic transformation of quartz particles results in damage to the sintered microstructure, counteracting the effect of tempering, i.e. mechanical strength does not increase as much as expected.

In many studies on triaxial porcelains [17–19], quartz is considered to play an important role in the resulting product properties. In porcelain tiles, this role is even more critical because quartz is the most abundant crystalline phase in the end product. On the one hand, the difference between the thermal expansion coefficients of the quartz and the matrix has a strengthening effect, since it subjects the matrix to a microscopic residual compressive stress that originates during the cooling phase of the industrial firing cycle. The effect of the other heat-treated body components is less significant, since their coefficients of thermal expansion are closer to that of the matrix. Recent studies have demonstrated the existence of such residual stresses in porcelain tile [20,21]. The magnitude of these microscopic stresses produces cracks around the quartz particles, causing stress relaxation and increasing microstructural damage, adversely affecting the product's mechanical behaviour. In these studies, the residual stress on quartz particles in porcelain tiles has been measured using X-ray diffraction [20]. The effect of quartz particle size on these residual stresses has also been analysed [21]. Since quartz expands more than the matrix, radial tensile stress develops in the particle–matrix interface and tangential compression occurs in the matrix. Fig. 10 shows a scheme of the macroscopic and microscopic stresses acting on the porcelain tile surface.

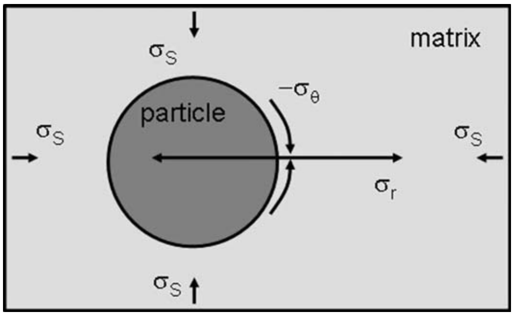


Fig. 10. Potential microscopic (σ_r, σ_θ) and macroscopic (σ_s) stress states on the porcelain tile surface.

The microscopic and macroscopic residual stresses in porcelain tile are extremely important, since they seriously affect tile mechanical properties and behaviour during the manufacturing process (for example, they are responsible for manufacturing defects such as cracks, breakage, and deformation, which entail severe economic losses). The determination and analysis of these residual stresses are key issues when it comes to optimising the manufacturing technology of this high-performance ceramic tile.

Glazed and unglazed porcelain tiles display so-called 'delayed curvatures', which consist of the change in tile curvature after the tiles leave the kiln. This phenomenon becomes more problematic as tile size increases. A recent study [22] has quantified the variation of curvature with time of industrial glazed porcelain tiles. Fig. 11 shows a plot of the evolution of tile deflection with time obtained in this study for two types of porcelain tiles. A change in curvature trend (concave–convex) can be observed in the tile, which exhibits delayed curvature. This means that there are two simultaneous, opposing mechanisms, with different kinetics, which influence the process.

Theoretical analyses indicate that only two factors can produce delayed curvatures: residual stresses and moisture expansion of the tile body. In both cases, additional

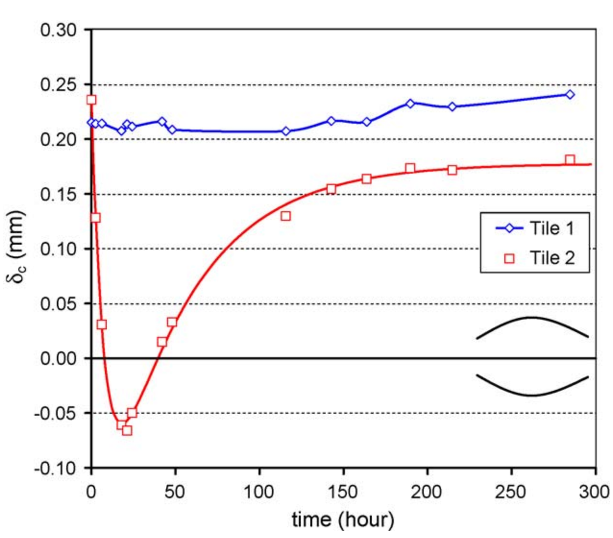


Fig. 11. Evolution of tile deflection (∂_C) with time for porcelain tile 1 without delayed curvature and porcelain tile 2 with delayed curvature.

circumstances need to occur for delayed curvatures to appear. Thus, for example, the presence of residual stresses is not synonymous with delayed curvatures, but an additional mechanism is needed that allows progressive liberation of these stresses, namely creep. In addition, the condition that the stress profile is not symmetrical with respect to the centre plane of the tile also needs to be obeyed.

In regard to the expansion of the bodies, special conditions must also occur for these to cause delayed curvatures. In particular, it is necessary for the expansion at the tile fair face and at the rib face to be different. Uniform expansion would lead to slight dimensional change, but not to delayed curvature, not even in the presence of glaze. Some of these differences stem from the rapid firing cycle in which the total amount of heat transferred to both sides of the tile is not exactly the same. Thus, for example, a difference of 0.1‰ in the expansion of a 410 mm × 410 mm size tile could cause a delayed curvature, expressed as a deflection, of about 0.3 mm. Although there are indications that suggest this difference exists, there are no conclusive results yet on this point.

The measurement of the factors that influence delayed curvatures is complex because different techniques from those typically used in characterising ceramic tiles are required. Procedures were fine-tuned in the above-mentioned study to measure the different factors that gave rise to delayed curvatures (Fig. 12). Since delayed curvature needed to be observed from the moment the tiles left the kiln, it was necessary to design and fine-tune a test procedure that would enable body expansion to be determined during that time. The main difficulty involved in the measurement was the temperature variation during the test, which might considerably affect measurement accuracy. In order to address these difficulties a device was built, shown in Fig. 12, which was able automatically to offset the temperature changes.

The residual stresses in the body stemming from the thermal gradients were measured using the strain relaxation slotting method (SRSM). This method consists of fixing a gauge to the bottom of the unglazed tile (Fig. 12), and then making increasingly deep cuts (a_i) from the top surface, measuring the strain recorded by the gauge (ε_g) (Fig. 13). In order to be able to calculate the residual stress profile it is necessary to know the relation between ε_g (a_i) and the stress at each point inside the piece. This relation is determined by certain calibration factors which need to be theoretically calculated for each geometry by a numerical method (in this case the finite element method was used). Finally, once the calibration factors have been determined, the stress profile can be calculated.

Polished unglazed porcelain tile production has drastically decreased in the last few years, as a result of the rapid adoption of glazed porcelain tile. However, research into the polishing process has been relatively significant in the last 10 years, due to the former lack of basic knowledge [23,24].

Previous studies on the polishing mechanism with differently sized abrasive particles focused on the influence of polishing conditions and the mechanical properties of the tile polishing tools [25]. The simulation of grinding work in porcelain tile polishing by means of a pilot polishing machine

Fig. 12. Left: device that automatically offsets temperature for the measurement of body expansion. Right: residual stress measurement test and detail of the gauge.

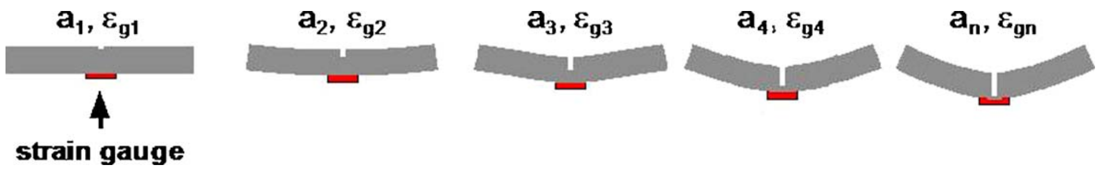


Fig. 13. Foundations of the strain relaxation slotting method (SRSM).

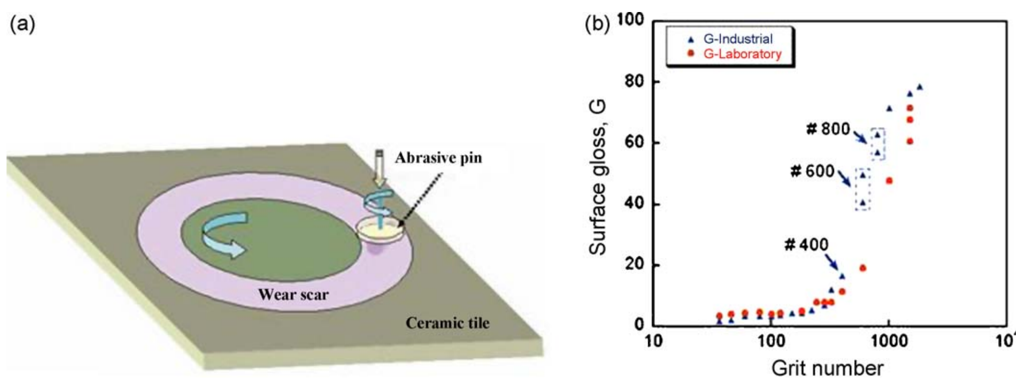


Fig. 14. (a) Sample and abrasive pin motion used in the laboratory tribometer. (b) Development of porcelain tile surface gloss with grit size for a laboratory tribometer and an industrial polishing machine.

equipped with sensors has also been reported [26]. That study further evaluated the impact of certain polishing machine variables on porcelain tile quality. The simulation of polishing time on the tile surface, based on kinematic equations, has also been addressed [27]. However, these studies did not provide detailed quantitative information on the development of the surface finish (in terms of roughness and optical gloss) during the polishing process. For this reason, a laboratory-scale tribometer was designed in the frame of a recent research study [28] to achieve a better understanding of this process. This equipment (Fig. 14a) allowed the characteristics of both the tiles and the abrasive polishing media to be quantitatively assessed. The results obtained by this apparatus, in terms of tile surface properties, are comparable with those observed in the large-scale polishing process used in an industrial polishing line (Fig. 14b) [28]. Thus, the effects of the process variables could be carefully studied and a model of porcelain tile surface evolution could be advanced [29,30].

3.3. Relationship between porcelain tile microstructure and certain tile properties

The factors that determine porcelain tile mechanical properties depend on tile composition and processing characteristics. Fig. 15 shows the variation of specimen mechanical properties (fracture strength σ_R, modulus of elasticity, E, and toughness, K_{IC}) with firing temperature [31]. All three properties show similar trends with firing temperature, and parallels can be drawn with the trend in sintered density (see Fig. 16). For the same starting composition, these mechanical properties all depend on the porosity of the fired piece, and therefore reach their peak

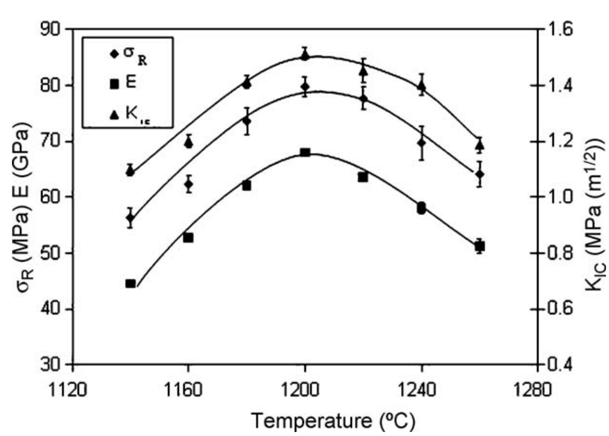


Fig. 15. Relation between mechanical properties (fracture strength σ_R, modulus of elasticity E, and toughness K_{IC}) and firing temperature for specimens obtained from an industrial porcelain tile powder.

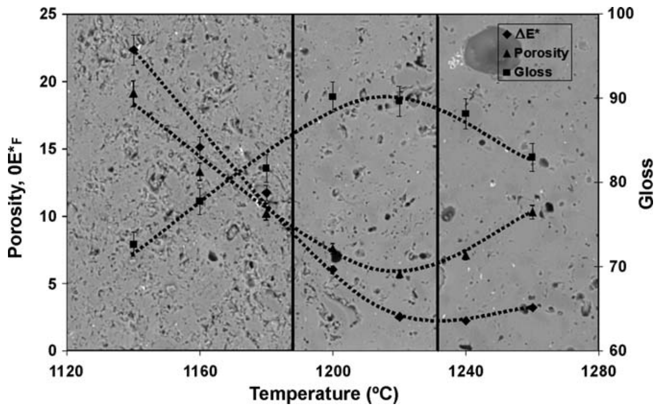


Fig. 16. Influence of firing temperature on porcelain tile surface characteristics of specimens obtained from an industrial spray-dried powder: porosity, irreversible stain retention (ΔE^*_{F}), and gloss after laboratory polishing.

values at the firing temperature which gives minimum porosity (1210 °C). Higher temperatures lead to specimen bloating, resulting in reduced strength and other mechanical properties. In this research, the weakening effect of porosity on the mechanical properties of porcelain tile has also been proved with different porcelain tile compositions prepared in the laboratory by changing quartz content and particle size.

In addition, factors other than porosity may affect porcelain tile mechanical properties. Thus, both the microstructural damage and the reinforcing mechanism stemming from the quartz particles can also decisively affect porcelain tile mechanical properties [20]. The effect of mullite on mechanical properties has also been addressed [32]. There are basically three theories that explain the strengthening mechanism in triaxial porcelains which may be applied to porcelain tiles, given the similarities between both materials: interconnection of acicular mullite crystals; dispersion of crystalline phases that limit the natural flaw size and causes diversion of the fracture path; and matrix strengthening as a result of the difference between the linear thermal expansion coefficients of the matrix and those of the disperse crystalline phases. These mechanisms act simultaneously, making it difficult to determine categorically which one contributes most.

Leonelli et al. [33] postulated that undissolved quartz crystals provide resistance to crack propagation by microcracking. In the second place, a crack deviation mechanism occurs in the vicinity of quartz grains. A. de Noni et al. have also recently confirmed the role of quartz in the porcelain tile reinforcing mechanism [20,21]. Quartz particles contribute decisively to increasing the fracture energy, either by increasing the state of compressive residual stress in the glass matrix associated with the thermal expansion mismatch with the glassy matrix or by promoting a combination of crack deflection and microcracking mechanisms. In contrast, the authors show that mullite and kaolinite glass significantly worsen the fracture energy, which counters the mullite hypothesis as a porcelain tile-strengthening mechanism.

The surface properties of the polished product, such as gloss or stain resistance, also depend on the level of surface porosity resulting from the polishing process [31,34,35]. In the case of stain resistance, pore size and geometry influence surface soilability and cleanability [36]. Fig. 16 shows the variation of ΔE^*_{F} (irreversible stain retention) and porosity with firing temperature as reported in the literature. ΔE^*_{F} represents the irreversible stain retention (i.e. the stain that cannot be removed by the cleaning process) and is an indirect measure of the product's stain resistance. ΔE^*_{F} varies in a similar way to porosity, displaying a minimum at a temperature slightly above T_{min} (temperature at which minimum porosity is achieved). The fact that ΔE^*_{F} does not increase above T_{min} in the same way as porosity is because, as Fig. 16 shows, the microstructure has changed from a matrix with irregularly shaped interconnected pores to a much more compact matrix with isolated round pores, which are easier to clean. For this reason, in industrial practice it is preferable to fire at a slightly higher temperature than T_{min} in order to avoid the pronounced drop in stain resistance (i.e. rise in ΔE^*_{F}) which results from underfiring.

On the other hand, as it is also readily observed in Fig. 16, the gloss level of a highly polished sample falls with the increase in porosity. The maximum attainable gloss depends on the microstructure of the material, which is defined by its composition and processing conditions. The dependence of gloss and stain resistance on porosity were also confirmed with porcelain tile specimens in which the quartz content and quartz particle size had been modified according to the industrial practice range [31].

All these findings indicate that at standard firing temperatures, the polished surface quality (gloss and stain resistance) depends on tile microstructure, which is in turn related to the starting composition (quartz content) and processing conditions (i.e. quartz particle size reduction by milling). It is therefore not surprising that products with very different qualities can be found in the marketplace, associated with highly varying microstructural characteristics.

Finally, in relation to the microstructural homogeneity of fired porcelain tile, close examination of a polished porcelain tile cross-section reveals a non-uniform distribution of the residual pores through the thickness, which results in a spatial gradient of properties. García-Ten et al. [37] have demonstrated the existence of these microstructural gradients through porcelain tile thickness by progressively polishing porcelain tile specimens in the laboratory to different depths, and observing them by optical microscopy (Fig. 17). These findings have recently been confirmed by Cannillo et al. [38] who postulate that a porcelain tile can be regarded as a functionally gradient material and, hence, modelled as a multilayered system. On the basis of simulation tools, these authors show that the porosity distribution through the tile thickness results in a spatial variation of elastic properties.

4. Future research lines

This last part of the paper reviews the R&D lines which, in the opinion of the authors, will witness further development in the short and medium term, development that will obviously parallel the technological advances of the product and its manufacturing process. For the sake of simplicity, these lines

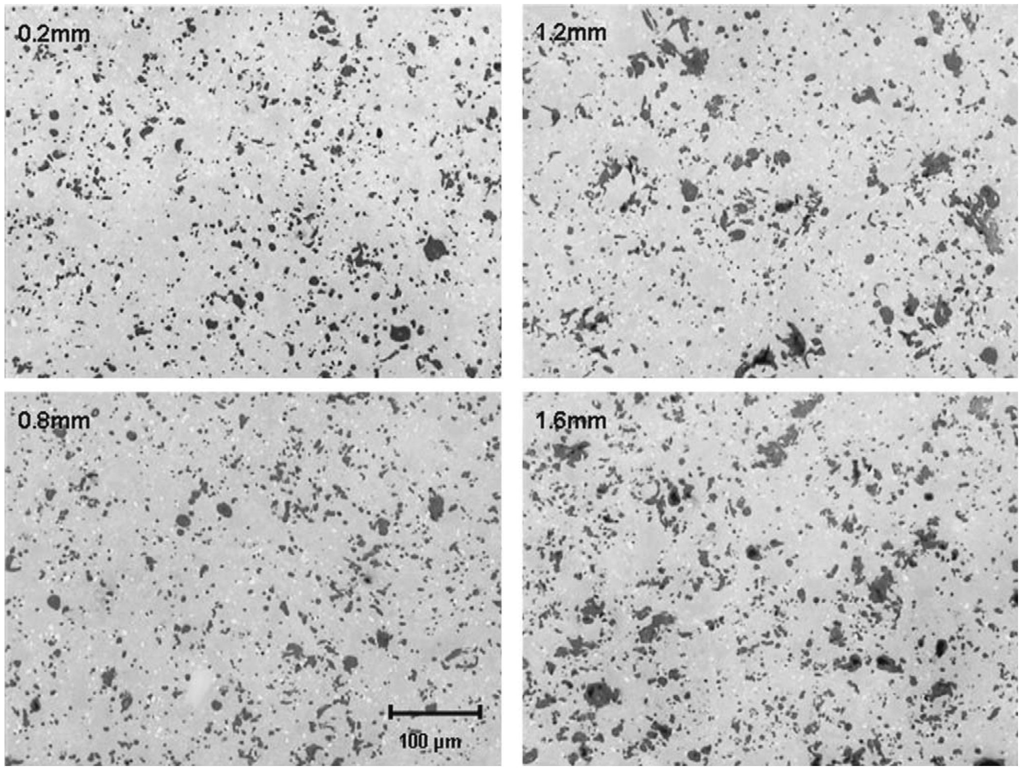


Fig. 17. Optical micrographs of porcelain tile specimens progressively polished to different depths in the laboratory (from 0.2 to 1.6 mm).

will be divided into the following three categories: new materials and compositions, novel functionalities and applications, and advanced technologies in the manufacturing process.

4.1. New materials and compositions

At present, the existing environmental and economic conditioning factors, the need to use natural resources better and to reuse the wastes generated in the own manufacturing processes, among other factors, are driving the search for alternative products and processes that allow conformity to the efficiency and sustainability criteria nowadays demanded by society. This search implies the reformulation of current compositions by the incorporation of new raw materials or additives. Thus, the dramatic rise in price of some key raw materials, such as Ukrainian clay, has increased the interest in purification processes for lower quality (and lower price) clays. Similarly, rising deflocculant costs may be offset by the design of compositions with lower clay material contents and small quantities of binder.

Recent studies, which have also sought to reduce manufacturing costs, have attempted to shorten the porcelain tile firing cycle by introducing highly fluxing additives [39] or wastes [40–42]. This research line will certainly be further pursued in the future.

Finally, also to be noted is the increasing research activity aimed at reusing porcelain tile polishing waste for making high value-added products, such as ceramic foams or lightweight ceramics [43].

4.2. Novel functionalities and applications

Nowadays, porcelain tile surface properties such as slip resistance or cleanability are highly demanded by the market in order to meet new and future safety and environmental regulations and legislation. Any improvement in the porcelain tile surface for flooring will need to balance slip resistance and other new functionalities, together with chemical and wear resistance, without impairing tile aesthetic appearance in terms of optical transparency, brightness, and smooth texture and feel. New, advanced surface functionalities such as easy-to-clean, self-cleaning or tunable (bioinspired) adhesion effects have attracted much recent interest in the scientific community [44–46]. Fig. 18 shows some of these targeted functionalities.

In order to design these new surfaces, nanomaterials and/or hybrid materials will be indispensable. At present, these novel materials are hardly used in ceramic tile manufacturing processes. It is therefore necessary to develop a completely new methodology in order to suitably choose, handle, and incorporate these materials into the ceramic tile surface with a view to obtaining the desired properties. Although certain porcelain tile products that accomplish a number of these functionalities are available in the market, much research still needs to be done to create processable and marketable advanced surfaces.

On the other hand, research has been ongoing for several years into new systems that facilitate the installation of porcelain tiles in order to reduce the cost and environmental impact of current systems. Various such commercial approaches are already available and have been presented at

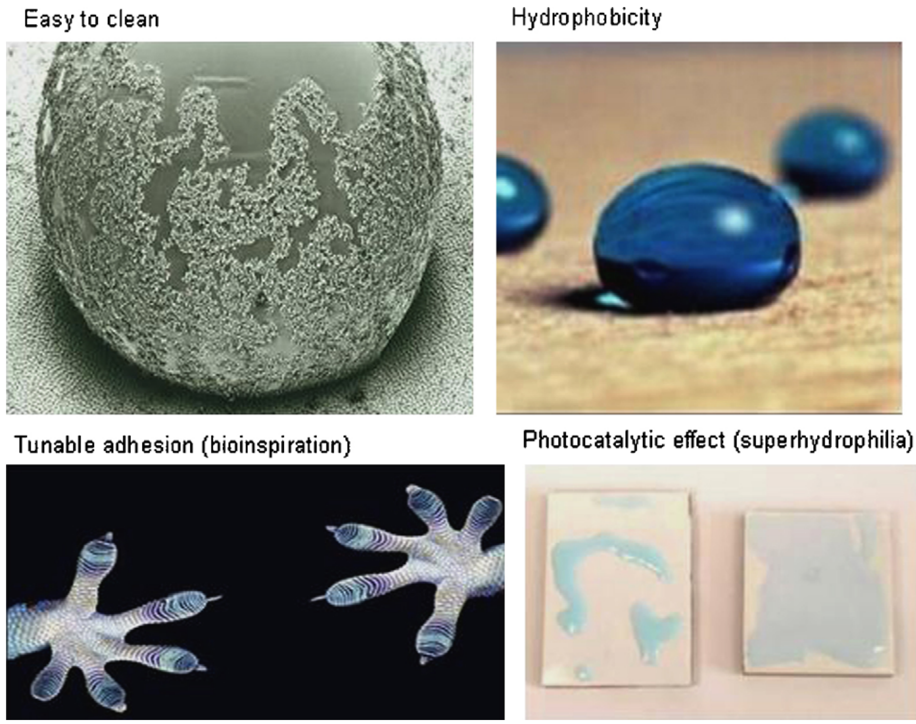


Fig. 18. Examples of targeted functionalities on porcelain tile surface.Source: http://nanotechweb.org/cws/article/tech/16392.

fairs or exhibitions. This line of research will undoubtedly be intensely pursed in coming years.

Ventilated façades represent a promising niche for ceramic tiles in general, and for porcelain tile in particular. Such systems exhibit excellent heat and acoustic insulation, in line with today's trend towards sustainable construction methods. In these systems the tiles are not directly adhered to the building walls, but are hung using mechanical clips. To develop this application it has been necessary to engineer customised new systems for the installation of large porcelain tile sizes in a safe and cost-competitive way. The application of porcelain tile in ventilated façades is already a reality that may be expected to undergo great development in coming years, in view of the great efforts in research and marketing currently being made by major porcelain tile manufacturers. An example of this pursuit is the research related to bioclimatic envelopes [47]. These envelopes, which are intended to enhance energy efficiency in buildings, represent a step forward in the concept of ventilated façades, as well as in the use of porcelain tiles in a highly sustainable environment. These bioclimatic envelopes are characterised by having three clearly differentiated areas or sectors: a heat capture sector, a heat transfer channel (HTC), and a stabilisation sector. The heat capture sector is made up of elements designed to absorb the solar radiation impinging on the envelope. The heat transfer channel is the duct behind the capture sector through which the trapped air, fed in through an aperture at the bottom of the envelope, rises as a result of free convection. The stabilisation sector, situated behind the HTC, is generally formed by a wall of high thermal mass which, apart from having a structural function, smoothes the temperature fluctuations that develop throughout the day at the inner face of the envelope. Sometimes the HTC may include insulation in order to maximise heat transfer towards the air circulating on the inside and minimise heat flow through the stabilisation sector.

The search for new applications has not only required investigation of new installation systems but the design of new products, such porcelain tile laminates, which may be up to 4 m long and just 3 mm thick [48]. This innovation focused initially almost exclusively on new applications of porcelain tile, differing from current uses, aimed at replacing materials such as wood, plastic, or metal in applications till now inaccessible to ceramics, such as a armoured doors or kitchen shelves, since the possible tile sizes that can be made are practically unlimited. However, the manufacturing process involved in fabricating these products has more recently focused on shaping thicker porcelain tile preforms, which are subsequently turned (cut) into more standard tile sizes in order to provide a more flexible manufacturing process in comparison with the current powder pressing technique [49].

The combination of these new products with new installation systems is also attracting much interest in construction. For example, Fig. 19 shows the building of the new University Jaume I auditorium in Castellón, Spain, whose ventilated façade are being developed with sheets of porcelain tile. Intense research work is currently ongoing with a view to implementing different decoration systems in the manufacturing process of these laminates. Other possibilities based on joining slabs with different properties are also under study, such as the use of polymers, plaster, fibre-reinforced ceramics,

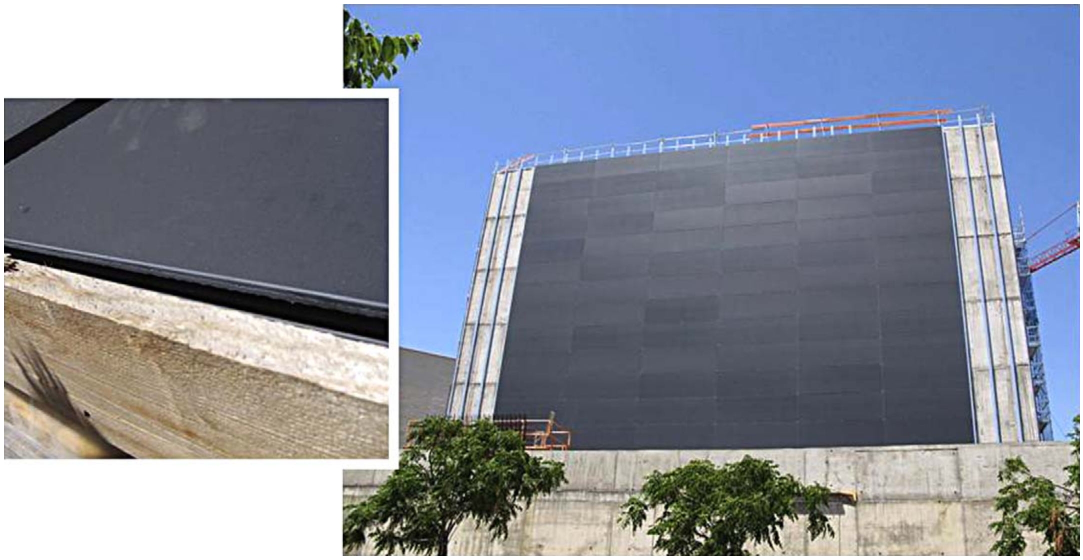


Fig. 19. Ventilated façade of the new auditorium building under construction at University Jaume I of Castellón (Spain). On the left, a detail of the porcelain tile laminate used (Laminam by Cerámica Saloni).

ceramic composites containing conductive layers (heating systems), or inner porous layers for thermal and acoustic insulation [50,51].

Finally, the installation of different types of sensors and control features in construction elements such as porcelain tiles, together with the possibilities of new communication technologies, opens up new potential avenues for equipping such items with functionalities that were until recently hardly imaginable. In addition, the development of new materials based on biotechnologies needs to be considered here, for example, embedded bioelectronics and materials with active surface properties. This is a line of work with enormous possibilities and applications, which could contribute to improving different aspects of daily life, from energy saving to ongoing attention to and watching over handicapped or dependent persons. The following are examples of embodiments of sensing applications and information and communication technologies (ICT) in porcelain tiles: integration of photovoltaic sheets, integration of sensors and walls capable of emitting sounds [51].

4.3. Advanced technologies in the manufacturing process

New simulation and modelling tools have today become indispensable, since they allow the feasibility of processes developed for the obtainment of new products to be analysed, and the predictability and efficiency of these processes to be enhanced by innovation in manufacturing, control, and measurement processes, the ultimate aim being quality assurance throughout the production batch, with manufacturing flexibility.

The aim of engineering more economic and sustainable processes has recovered former approaches related to powder preparation, such as the dry route method. A recent intense research effort has allowed the development of high-efficiency mills and granulators suitable for this process [52]. The benefits in terms of decreased water and energy consumption are evident. An adaptation of the starting compositions is also necessary. However, finished product quality, in comparison with that obtained from the current wet route, still needs to be proved, in particular with porcelain tiles.

A great number of non-contact decorating systems, such as inkjet printing, are progressively being incorporated into the manufacturing process. Ceramic inkjet printing was first developed some years ago [53] and many other such techniques are now in the industrial implementation phase. This technology has required and will, in the future, need further adaptation of the solids used in the ink formulation, taking into account emerging nanoparticle synthesis technology.

Finally, with regard to tile finishes, the advance of glazed porcelain tile has led to significant changes in the polishing process. Thus, highly intensive polishing on the whole surface of the unglazed porcelain tile to several tenths of a millimetre has been progressively replaced with a much less intensive mechanical surface treatment in terms of material removal. This evolution has materialised through extensive modification of the polishing technology and, in particular, of grinding tool characteristics, which will require further research in the future.

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